978. *The Production of Active Solids by Thermal Decomposition. Part XII.* The Calcination of Hydrous Titania.*

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The effect of heat treatment on certain properties of hydrous titania prepared by the hydrolysis of the sulphate has been studied. Separate samples of the titania have been calcined for 5 hr. at a series of temperatures (*T*), and a number of properties of the cooled product (including specific surface, pore volume, and adsorption of water and of benzene) have been measured. The specific surface diminishes continuously with increasing temperature of calcination, but the pore volume shows little change below 600°; between 600° (which is probably close to the Tammann temperature) and 1000° the loss of specific surface is accelerated and the pore volume diminishes markedly. When, between 970° and 1100°, the conversion of anatase into rutile occurs, the loss of specific surface is decelerated and the pore volume actually increases somewhat, both effects probably resulting from the contraction in the true volume of the material.

The surface of the specimens immediately after calcination is in part oxide and in part hydroxide; the proportion of the latter diminishes as the temperature of calcination increases. Exposure to moist air or water vapour slowly converts the oxide into hydroxide.

In Part I[1] it was pointed out that calcination of a hydrous oxide should yield an active solid with an activity diminishing continuously as the temperature of calcination increased;

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* Part XI, *J.*, 1960, 1162.

[1] Part I, Gregg, *J.*, 1953, 3940.

and, in later Parts, examples of this type of behaviour (*viz.*, ferric oxide,[2] silica,[3] and stannic oxide [4]) have been described; in the present Part a further example, titania, is dealt with, an added feature of interest being the occurrence at red heat of a polymorphic transition (from anatase to rutile) which might be expected to produce an activating effect.

EXPERIMENTAL

Materials.—The hydrous titania was a " pulp " kindly provided by Mr. J. T. Richmond. It had been prepared from crushed ilmenite which had been dissolved in concentrated sulphuric acid and purified. The resulting solution, which contained *ca.* 230 g. of titania per l. (presumably as basic sulphate), was then heated to cause hydrolysis; the pulp was filtered off, washed with dilute ammonia solution to remove the anionic impurities as far as possible, and air-dried. The analysis of the pulp before washing was (p.p.m.): Fe_2O_3, 100; Cr_2O_3, 8; V_2O_3, 8; Sb_2O_3, 0·1; and (%) PO_4, 0·35; SO_4, 0·38. Both thermogravimetric analysis and direct determination by ignition showed that the content of volatile impurity after the pulp had been washed was 0·5%.

Procedure.—The procedure was substantially that adopted in previous Parts. The titania pulp was heated, in separate portions, each at a separate fixed temperature, for 5 hr., and the following properties of the cooled solid were measured: adsorption of nitrogen at −183° by a volumetric method [5] to calculate the specific surface (the sample was outgassed overnight, at 115°); the adsorption of benzene vapour and of water vapour by use of an electromagnetic sorption balance; [6] the density by immersion in carbon tetrachloride (ρ_{CCl_4}) [7] and in mercury (ρ_{Hg}) [8] to calculate the pore volume V ($=1/\rho_{Hg} - 1/\rho_{CCl_4}$); the X-radiogram with Cu-K_α radiation; and the water content by the thermogravimetric analysis.

RESULTS AND DISCUSSION

Below 900° the X-ray pattern of the samples was that of anatase with broadened lines, and the increase in temperature merely led to a sharpening of the lines, signifying an increase in crystallite size. The conversion into rutile was confined effectively to the range 950—1100° (Fig. 1, Curve *a*). This is supported by the figures for ρ_{CCl_4} (Fig. 1, Curve *b*) which show an increase from 3·9 g. cm.$^{-3}$, corresponding to anatase, to nearly 4·3 g. cm.$^{-3}$, corresponding to rutile, in this temperature range.

For discussion it is accordingly convenient to divide the results into those for the temperatures below and above 950°.

The curve for specific surface below 950° shows a continuous fall (Fig. 2). There is no maximum, in accordance with the fact that titania gel is a hydrous oxide,[9] and (as confirmed by the X-ray results) it does not change its lattice when water is driven off: rise in temperature produces sintering but no activation. At about 600°, however, the sintering begins to accelerate, as is clear from Fig. 3, where log S' is plotted against $1/T$ [S' = surface area per g. of TiO_2; T = temperature (°K) of calcination].

The pore volume V (Fig. 4), which varies but little below 600°, falls rapidly between 600° and 1000°; the ratio $V : S$ which is proportional to the average pore width d (for cylindrical pores $d = 4V/S$) increases continuously with rise in temperature of calcination (Table 1). Thus below 600° the mechanism of sintering must be such as to reduce the surface area whilst keeping the pore volume constant; and it must consist in a disappearance of the finer pores without disturbance of the framework of the grains, the eliminated volume being merely added to the volume of the larger pores (cf. Part XI [4]). This picture

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[2] Gregg and Hill, *J.*, 1953, 3945; Goodman and Gregg, *J.*, 1956, 3612.

[3] Goodman and Gregg, *J.*, 1959, 694.

[4] Goodman and Gregg, *J.*, 1960, 1162.

[5] Sing, Ph.D. Thesis, London, 1949; Tompkins and Young, *Trans. Faraday Soc.*, 1951, **47**, 77.

[6] Gregg, *J.*, 1955, 1483.

[7] Culbertson and Dunbar, *J. Amer. Chem. Soc.*, 1937, **59**, 306.

[8] Asher, Ph.D. Thesis, London, 1955.

[9] Weiser, Milligan, and Cook, *J. Phys. Chem.*, 1941, **45**, 1226.

TABLE 1. *Ratio of pore volume* (V *cm.*^{3} *g.*$^{-1}$) *to surface area* (S *cm.*^{2} *g.*$^{-1}$).

Temp. of calcination (°c) ...	205	306	406	505	595	746	810	939
$V \times 10^6/S$ (cm.)	0·58	0·74	1·2	1·3	1·4	2·5	3·8	5·8

is consistent with the gradual increase in the value of $V:S$ (Table 1). These changes could occur without much alteration in the shape of the actual crystallites themselves, for the surfaces of adjacent crystallites could join if the crystallites moved slightly relative to their immediate neighbours. The marked reduction in pore volume which commences at about 600° indicates that the framework is now collapsing, and this must involve some alteration in shape (by viscous or plastic flow [10]) of the crystallites. With many oxides and metals a sharp increase in flexibility or plasticity sets in at a characteristic temperature,

FIG. 1. *The rutile content* (*Curve a*) *and the density* (*Curve b*) *of calcined titania.*

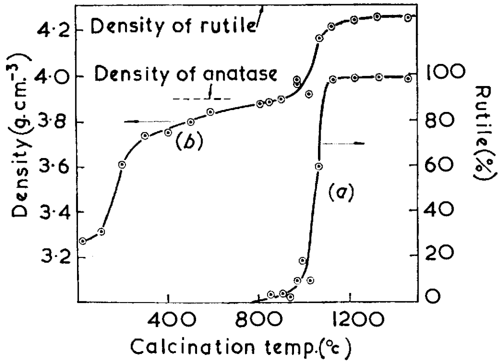


FIG. 2. *The specific surface of calcined titania.* (*Separate specimens were calcined for* 5 *hr. at each temperature.*)

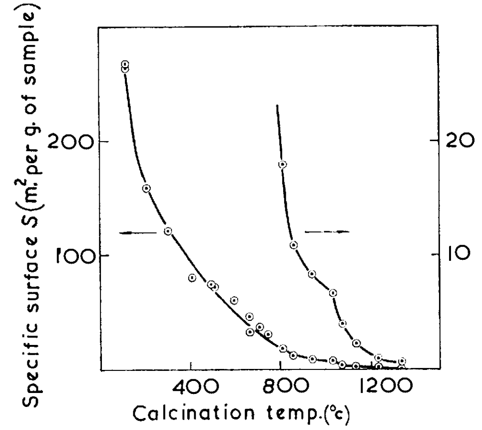


FIG. 3. *Plot of log S′ against* 1/*T.* [*S′ = surface area per g. of* TiO$_2$; *T = temp.* (° K) *of calcination.*]

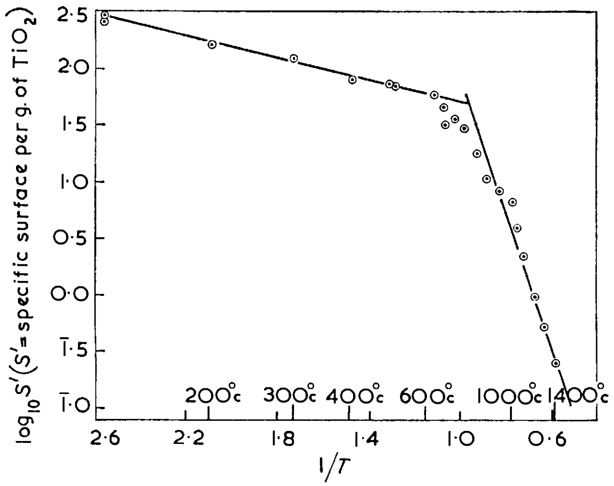
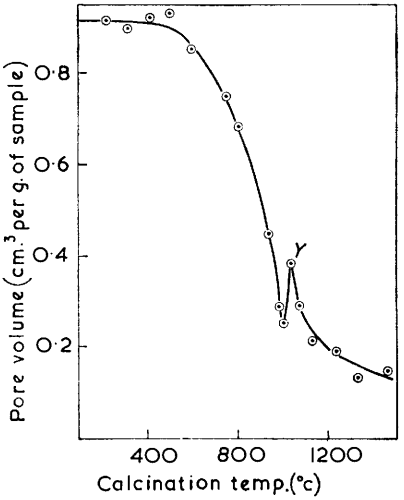


FIG. 4. *The pore volume of calcined titania.* (*Separate specimens were calcined for* 5 *hr. at each temperature.*)



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[10] Clark, White, and Cannon, *Trans. Brit. Ceram. Soc.*, 1953, **52**, 1.

the Tammann temperature,[11] which varies from one substance to another within the range 0·37—0·52T_m [T_m = m. p. (°K) of substance]; the temperature 600°, at which the collapse of the framework commences, corresponds to 0·42T_m (since the m. p. of rutile is 1825°) and so could be at or near the Tammann temperature of the substance.

The sorption isotherms (Figs. 5 and 6) lend general support to these views. The benzene isotherm for the 117° sample below a relative pressure of 0·7 is characteristic of an adsorbent with pores having a width of a very few molecular diameters;[12] the steep rise at relative pressures above 0·80 or so is typical of capillary condensation in large pores ($d > 200$ Å, say)[13] or in interstices between the grains. For temperatures from 205° to 595° there are hysteresis loops which move progressively towards higher pressures as the temperature of calcination increases, consistently with a gradual increase in the pore radius. [The pore

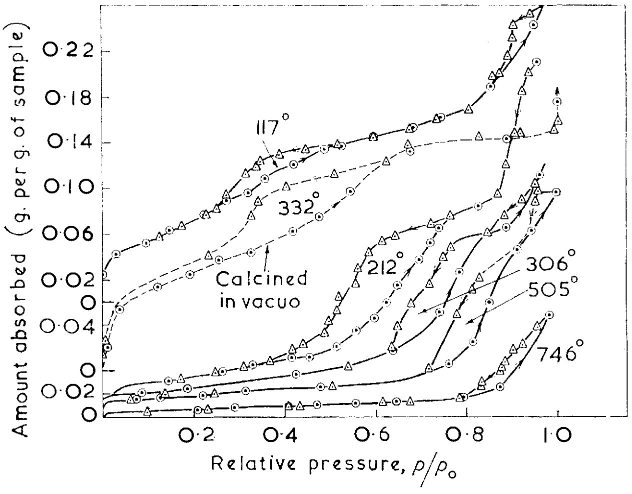

FIG. 5. *Adsorption isotherms of water vapour at 23° on calcined titania.*

(*The temperature of calcination is marked on each isotherm. The zero of the* 332° *isotherm is displaced upwards by* 0·04 *g. and that of the* 117° *isotherm by* 0·010 g. *Circles denote adsorption, triangles desorption.*)

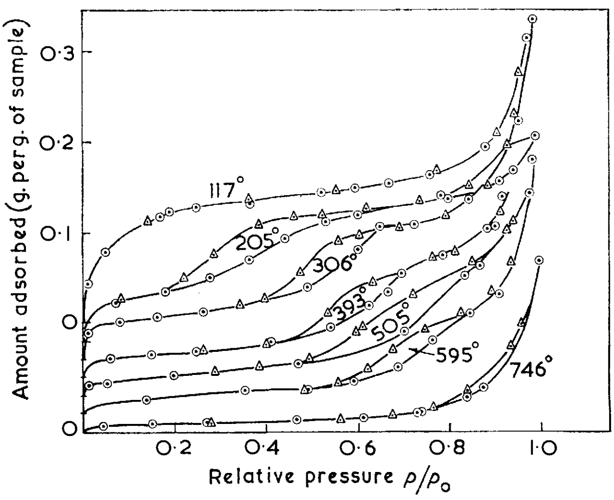

FIG. 6. *Adsorption isotherms of benzene vapour at 23° on calcined titania.*

The temperature of calcination is marked on each isotherm. The zero of the isotherms reading from below upwards is successively displaced vertically by 0·02 *g. Circles denote adsorption, triangles desorption.*)

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[11] Finch and Sinha, *Proc. Roy. Soc.*, 1957, *A*, **239**, 145.

[12] Pierce, Wiley, and Smith, *J. Phys. Chem.*, 1949, **53**, 669.

[13] Cf. Foster, *Trans. Faraday Soc.*, 1932, **28**, 645.

radii (in Å) calculated by the Kelvin equation for the inception (r_i), inflexion ($\bar{r}$), and closure (r_c), of the loops, given below, illustrate this]:

Pore radius (Å).

Temp. (° c)	212	306	393	505	595	740
r_i	13	22	24	28	31	54
$\bar{r}$	18	30	35	50	51	—
r_c	45	50	56	170	140	400

The water isotherms, though slightly more complicated, give evidence pointing in the same direction.

In the range 950—1100° the conversion of anatase into rutile occurs (Fig. 1) and it is associated with certain well-marked features in the measured properties.[14] Thus the loss in specific surface is much slower (Fig. 2) and the pore volume actually *increases* in the middle of this temperature range (Fig. 4).

These effects most probably result from the reduction in the true volume of the material which accompanies the transformation of anatase (*d* 3·9 g. cm.$^{-3}$) into rutile (*d* 4·3 g. cm.$^{-3}$). The phase change will proceed from a finite number of nuclei of rutile which will start to grow at different times; the contraction will thus be non-uniform within the sample and must lead to the formation of new gaps and the extension of old ones. Additional surface will thereby be produced, but loss of surface by sintering will still be taking place, though more slowly because of the increase in the gaps between the crystallites; the net result is to diminish the slope of the curves of surface area against temperature and of pore volume against temperature.

In places, the stresses produced by contraction would be sufficiently severe to bring about the actual disintegration of the grain; and this explains the visual observation that a sample, calcined to 1070° and known to contain 60% of rutile and 40% of anatase, consisted of a mixture of large white lumps (*ca.* 1 mm. across) and a fine greyish powder; *X*-ray analysis showed the lumps to be pure anatase but the powder to contain ~65% of rutile. The formation of fine powder accounts for the increase in pore volume at *Y* (Fig. 4), since the mercury used in the determination cannot penetrate into the voids between fine particles [15] and so gives an anomalously high value for pore volume.

Since the phase change of anatase to rutile must involve some movement of ions, it might be expected to commence at the Tammann temperature rather than 200° above it, as in the present study. The delay is almost certainly to be ascribed to one or more of the impurities which are present, for with material of high purity the change does commence in the neighbourhood of the Tammann temperature (Part XIII); † and the anatase–rutile transformation is known to be highly sensitive to certain additives. Which particular impurity or impurities is or are responsible in the present case is as yet uncertain, however.

The Rôle of Water.—The water content gradually diminishes over a wide range of temperature, but even at 500° it is still appreciable (see Table 2). The water is evidently bound to the titania with a wide range of energies—as molecular water if it is expelled below 100°, as hydroxyl groups if it can only be expelled at temperatures approaching 300° or 400°, and perhaps by hydrogen bonds if it is driven off between 100° and 300°. Values

TABLE 2. *Water content.*

Temp. of calcination (°c)	117	205	306	406	505	595
Water content (%)	9·7	2·4	0·9	0·25	0·13	0
θ *	1·65	0·74	0·37	0·15	0·1	0

* θ = fraction of surface covered with water.

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† In the press.

[14] Barksdale, "Titanium, its Occurrence, Chemistry and Technology," Rheinhold Press, New York, 1949.

[15] Shapiro and Kolthoff, *J. Phys. Colloid Chem.*, 1948, **52**, 1020.

for the fraction θ of the surface covered, a cross-sectional area of 7·5 Å^2 being assumed for an OH group, are given in Table 2.

The isotherms of water on samples which have been calcined in vacuum (cf. the curve for 332°, which is typical, in Fig. 5) show that some water is retained, even after many hours of pumping, at the end of the desorption run.[16] This retained water is probably chemisorbed on parts of the surface which had lost their hydroxyl groups during the calcination; the retention is explicable in terms of a conversion of surface oxide into surface hydroxide groups during the progress of the adsorption experiment. The conversion is relatively slow—as one would expect since it would almost certainly be an activated process—for the amount of retained water is much too small to raise the value of θ to unity. In the sorption isotherms of water on the standard samples—*i.e.*, those which had been calcined in air and then exposed to humid air during storage—the retention effect was absent (Fig. 5); evidently the normal outgassing procedure (115° for 5 hr.) leaves the surface completely covered with hydroxyl groups.

TABLE 3. *Effect of different conditions during outgassing, on surface area.*

Temp. of outgassing (°c)	25	25	60	82	110
Time of outgassing (hr.)	5	*	*	5	5
Volatile matter (%)	13·8	9·5	7·3	7·5	6·2
S' (m.^{2} per g. of TiO_2)	211	199	183	316	311

* Until no further loss in weight.

At temperatures below 110° the percentage of water lost by outgassing increases with increase in both temperature and time of outgassing (Table 3); the surface area also changes, and the results can be explained in terms of two opposing processes—a removal of water from surface previously blocked, which tends to increase the area, and a sintering which tends to diminish the area.

We thank Messrs. Laporte Titanium Ltd. for a maintenance grant to one of us (R. C. A.) and for a grant towards the purchase of apparatus. Thanks are also offered to Mr. J. T. Richmond for supplying the titania pulp and for providing the *X*-ray diffraction results on the calcined samples.

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[16] Rao, *J. Phys. Chem.*, 1941, **45**, 500; *Current Sci.*, 1940, **9**, 70; Weiser, Milligan, and Simpson, *J. Phys. Chem.*, 1942, **46**, 1051.